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# DIVISION S-4—SOIL FERTILITY & PLANT NUTRITION

## Phosphorus Behavior in Flooded-Drained Soils. I. Effects on Phosphorus Sorption

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### ABSTRACT

**This study examines the effects of flooding periods (FP), organic-matter (OM) addition, and temperature changes during soil flooding on P sorption in 10 flooded-drained (FD) California soils. The soils were flooded for 0 to 90 d, drained, air dried, and used for P-sorption studies at six (0.3–2.0 m*M*) initial P concentrations ($P_i$). Four soils, showing a wide variation in P-sorption capacity, were evaluated for the effects of OM and temperature treatments. Using P-sorption isotherms, a relationship between P sorption and FP was developed for a given final P concentration ($P_f$) for each soil. Flooding soil without added OM increased P sorption by 10 to 70% in half of the 10 soils. Organic-matter treatment and elevated temperature during flooding further increased P sorption and shortened the FP at which P sorption reached maxima. The soils in which P sorption did not increase without OM treatment were low in either OM or reducible Fe. The largest increase in P sorption as a result of OM and temperature treatments was found in a soil that had low OM but a high level of reducible Fe. These findings suggest that OM and temperature are important factors determining the impact of FD conditions on P sorption.**

IN EARLIER STUDIES, we reported that flooding and subsequent draining of soil affected P transformations (Sah and Mikkelsen, 1986a), increased amorphous-Fe levels and P sorption (Sah and Mikkelsen, 1986c,d), and induced P deficiency in crops grown after flooded rice (*Oryza sativa* L.). We also reported that elevated soil temperatures increased P sorptivity and decreased the concentration of water-soluble P in FD soils (Sah and Mikkelsen, 1986b,c).

Application of OM to upland (aerobic) soils generally decreases P sorption (Frossard et al., 1986; Meek et al., 1979; Reddy et al., 1980; Kuo, 1983). Cellulosic OM added before flooding increased amorphous Fe concentrations in the FD soils (Sah and Mikkelsen, 1986d). Several Fe forms in soil are reported to correlate with P sorption (Khalid et al., 1977; Willet and Higgins, 1980; Kuo and Mikkelsen, 1979; Maraikar et al., 1983; Torrent, 1987), but the relationship of P sorption with changes in Fe forms under FD condition is not well understood.

The process leading to increased immobilization of P in FD soils perhaps starts during the FP of soil. The decrease in redox potential of flooded soils (Ponnamperuma, 1972; Sah et al., 1989; Gotoh and Patrick, 1974) causes transformation of several chemical species (Mandal, 1961; Khalid et al., 1978; Ponnamperuma, 1977; Savant and Kibe, 1969; Patrick et al., 1985). Reversal of these processes after soil drainage leads to increased chemical reactivity of soil minerals with P (Sah and Mikkelsen, 1986a–e), which may immobilize P for several years (Willet and Higgins, 1978, 1980; Sah and Mikkelsen, 1986f). A FP as short as 2 to 4 d increased P sorptivity in FD soils (Willet, 1982); however, the rate and magnitude of increased P sorptivity in FD soils is not fully explained by the duration of FP alone. Factors such as added OM and favorable soil temperatures that accelerate soil anaerobiosis (Sah et al., 1989; Patrick and Wyatt, 1964) may also enhance P sorption. Therefore, to examine the effects of FP on P sorptivity, OM and temperature must be taken into account. How these factors interact with FP and affect P sorption under FD conditions has not been elucidated.

This study examined the interactive effects of OM, temperature, and FP on P sorption in 10 soils representing variations in soil properties that were believed to be associated with the phenomenon of induced P deficiency in FD soil.

### MATERIALS AND METHODS

Ten soils were collected from northern California, where all except Soil 9 (Aiken clay) had been previously used for rice-based cropping systems but had not been flooded in the last 2 to 3 yr. Classification and relevant properties of these soils are reported in Table 1. To simulate FD soil conditions, 100-g samples of each soil were incubated under flooded conditions at 23 °C for 0 to 90 d. At the completion of the FP, the soils were drained and air dried at room temperature for 20 d to achieve aerobic conditions. Air drying at room temperature is not as extreme a condition as field drying, but it was used to provide standard conditions for attaining soil aerobiosis. The air-dried FD soils were ground to pass a 0.5-mm sieve. The P-sorption studies were conducted using FD soils at 20 d after soil drainage.

Two-gram FD soil samples were weighed into 50-mL polypropylene centrifuge tubes to which 30 mL 0.01 *M* $CaCl_2$ containing 0.3, 0.6, 0.9, 1.2, 1.5, and 2.0 m*M* P ($P_i$) as $KH_2PO_4$, and two drops of toluene were added to control microbial activities. The tubes were shaken on a reciprocating shaker for 0.5 h and incubated at a constant temperature of 23 °C for 6 d with 0.25-h shaking each day. After the incubation period, the tubes were again shaken for 1.0 h, centrifuged at 2500 rpm for 0.25 h, and clear supernatant liquid was filtered through Whatman no. 1 paper to remove any particulate matter. Phosphorus concentration in the filtrate was determined using the ascorbic-acid method (Watanabe and Olsen, 1965). Effects of FD conditions on equilibrium (final) P concentration ($P_f$) and P sorption were examined.

Four soils (no. 1, 2, 3, and 6), representing variation in soil properties and P-sorption capacities in FD soils (without OM treatment), were selected to evaluate the effects of FP, OM, and temperature. Soil 1 and 6 showed a large response,

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**Table 1. Classification and properties of the 10 soils used.**

| Soil series | Organic matter | pH† | $CaCO_3$ | Cation exchange capacity | Fe oxides | | |
|---|---|---|---|---|---|---|---|
| | | | | | FeA‡ | FeB§ | FeD¶ |
| | g kg$^{-1}$ | pH† | g kg$^{-1}$ | cmol$_c$ kg$^{-1}$ | | g kg$^{-1}$ | |
| 1. Gridley c | 18.8 | 5.2 | <0.5 | 10.46 | 0.50 | 1.29 | 6.34 |
| 2. Stockton c | 19.5 | 5.0 | <0.5 | 25.21 | 1.28 | 4.99 | 4.37 |
| 3. Yokohl c | 14.6 | 4.4 | <0.5 | 15.24 | 1.01 | 7.18 | 12.06 |
| 4. Genevra c | 16.7 | 8.0 | 8.0 | 20.26 | 0.44 | 3.21 | 9.10 |
| 5. Yokohl c (10–20 cm depth) | 11.1 | 5.2 | <0.5 | 12.89 | 0.53 | 5.16 | 1.32 |
| 6. Myers c | 17.4 | 6.3 | <0.5 | 31.47 | 0.40 | 3.02 | 10.18 |
| 7. Stockton c (dark phase) | 22.9 | 7.5 | 29.2 | 36.61 | 0.09 | 0.92 | 0.50 |
| 8. Capay c | 23.6 | 6.6 | <0.5 | 27.04 | 0.67 | 4.08 | 9.52 |
| 9. Aiken c | 11.1 | 5.4 | <0.5 | 31.91 | 0.38 | 1.41 | 41.02 |
| 10. Sacramento c | 11.8 | 7.8 | 6.8 | 27.43 | 0.53 | 1.97 | 7.00 |

Taxonomic classification:

1. Fine, montmorillonitic, thermic Typic Argixeroll
2. and 7. Not classified because of original broad or vague definition
3. and 5. Fine, montmorillonitic, thermic Typic Durixeralf
4. Fine, montmorillonitic, frigid Calcic Argixeroll
6. Fine, montmorillonitic, thermic Entic Chromoxerert
8. Fine, montmorillonitic, thermic Typic Chromoxerert
9. Clayey, oxidic, mesic Xeric Haplohumult
10. Very fine, montmorillonitic, thermic Vertic Haplaquoll

† pH = pH of saturated paste.
‡ FeA = Amorphous FeA, extracted with ammonium oxalate at pH 6 for 2 h.
§ FeB = Amorphous FeB, extracted with ammonium oxalate at pH 3 for 2 h
¶ Fe$_D$ = Free Fe oxides, extracted with dithionite-citrate-bicarbonate reagent.

**Table 2. Change in equilibrium (final) P concentration ($P_f$) of five soils at two selected initial P concentrations ($P_i$) as affected by the periods of soil flooding without added organic matter at 23 °C.**

| Soil no. | $P_i$ | Days of flooding 0 | 5 | 10 | 15 | 25 | 40 | 60 | 90 |
|---|---|---|---|---|---|---|---|---|---|
| | m$M$ | $P_f$, $\mu M$ P | | | | | | | |
| 1 | 1.2 | 831 ± 25† | 830 ± 0 | 750 ± 16 | 670 ± 8 | 610 ± 22 | 520 ± 0 | 530 ± 8 | 550 ± 8 |
| | 2.0 | 1540 ± 17 | 1580 ± 17 | 1460 ± 0 | 1320 ± 18 | 1270 ± 8 | 1170 ± 17 | 1180 ± 12 | 1180 ± 8 |
| 2 | 1.2 | 290 ± 2 | 250 ± 0 | 270 ± 8 | 240 ± 6 | 220 ± 4 | 205 ± 8 | 200 ± 4 | 200 ± 0 |
| | 2.0 | 770 ± 8 | 780 ± 17 | 770 ± 0 | 620 ± 14 | 600 ± 8 | 570 ± 4 | 590 ± 8 | 600 ± 12 |
| 4 | 1.2 | 410 ± 4 | 360 ± 4 | 340 ± 8 | 330 ± 0 | 350 ± 4 | 310 ± 4 | – | 260 ± 8 |
| | 2.0 | 960 ± 8 | 940 ± 8 | 830 ± 8 | 800 ± 0 | 810 ± 17 | 760 ± 0 | – | 640 ± 0 |
| 6 | 1.2 | 830 ± 4 | 410 ± 3 | 390 ± 4 | 370 ± 0 | 380 ± 8 | 360 ± 0 | 340 ± 4 | 310 ± 0 |
| | 2.0 | 1040 ± 8 | 1000 ± 12 | 950 ± 9 | 890 ± 42 | 910 ± 8 | 910 ± 0 | 830 ± 8 | 790 ± 8 |
| 8 | 1.2 | 173 ± 5 | 168 ± 8 | 162 ± 12 | 148 ± 6 | 159 ± 4 | 146 ± 4 | – | 129 ± 12 |
| | 2.0 | 570 ± 8 | 580 ± 0 | 580 ± 8 | 530 ± 16 | 550 ± 16 | 540 ± 8 | – | 480 ± 8 |

† Values following ± sign are standard deviation.

Soil 2 a small response, while Soil 3 had no response of P sorption to FD conditions (Table 2; Fig. 1b). Soil 1 and 6 had lower ratios of amorphous to free Fe oxides; Soil 1 had a lower CEC and pH than Soil 6. Soil 2 and 3 had higher ratios of amorphous to free Fe oxides; Soil 3 had three-fold more free Fe oxides but a lower CEC and OM than Soil 2 (Table 1). We selected Soil 3 to test the hypothesis that its lack of response to FD conditions was possibly due to its low OM content, which limits bacterial activity affecting anaerobiosis.

The four selected soils were amended with 10 g OM (85% cellulose + 15% starch) kg$^{-1}$ soil. Ten-gram samples of OM-amended soils were flooded in 50-mL centrifuge tubes (4 replications) for a period of 0 (unflooded) to 90 d at 23 and 35 °C constant temperatures. During incubation, the tubes were kept uncapped but covered with aluminum foil to reduce evaporation while allowing gas exchange. After the appropriate FP, the tubes were air dried at room temperature for 20 d, ground (four replications pooled) to pass a 0.5-mm sieve, and used for the P-sorption study. The P-sorption studies were conducted as discussed earlier (two replications) using 0.3, 0.6, 0.9, 1.2, 1.5, and 2.0 m$M$ $P_i$ for Soil 1 and 6 and 1.2 and 2.0 m$M$ $P_i$ for Soil 2 and 3 (due to limited facilities. $P_f$ for Soil 2 and 3 at $P_i$ = 0.3 was too low to be detected).

Langmuir isotherms were fitted to the P-sorption vs. $P_f$ data for each FP for Soil 1 and 6. From these isotherms, the expected P sorption (EPS) for $P_f$ values of 10, 50, 100, and 250 $\mu M$ were determined. The EPS values at equimolar $P_f$ values were plotted against the FPs and a curvilinear model, $Y = A(1 - b\ \exp^{-cx})$, was fitted to describe the relationship between EPS and FP, where $Y$ = EPS, $A$ = maximum EPS, $b$ and $c$ are constants, and $x$ = FP. In the above model, $Y$ asymptotically approaches $A$ if $x$ is very large. Therefore, the FPs were evaluated at $0.95A$ (i. e., 95% of the maximum EPS). At $Y = 0.95A$, $(b\ \exp^{-cx}) = 0.05$, and thus, $x = (1/C)(\ln b - \ln 0.05)$.

The effects of FP plateaued (0.95 of maximum) between 10 and 66 d for Soil 1 (Fig. 2) and between 30 and 65 d for Soil 6 (Fig. 3), depending on OM and temperature treatments. Phosphorus sorption at a series of $P_f$s were estimated at these FPS (where EPS = $0.95A$) and used to construct P-sorption isotherms (P sorption vs. $P_f$). The effects of OM and temperature treatments were studied on the P sorption isotherms of Soil 1 and 6.

## RESULTS AND DISCUSSION

### Effect of Soil Types

When soils were flooded without OM added, P sorption did not increase under FD conditions in 5

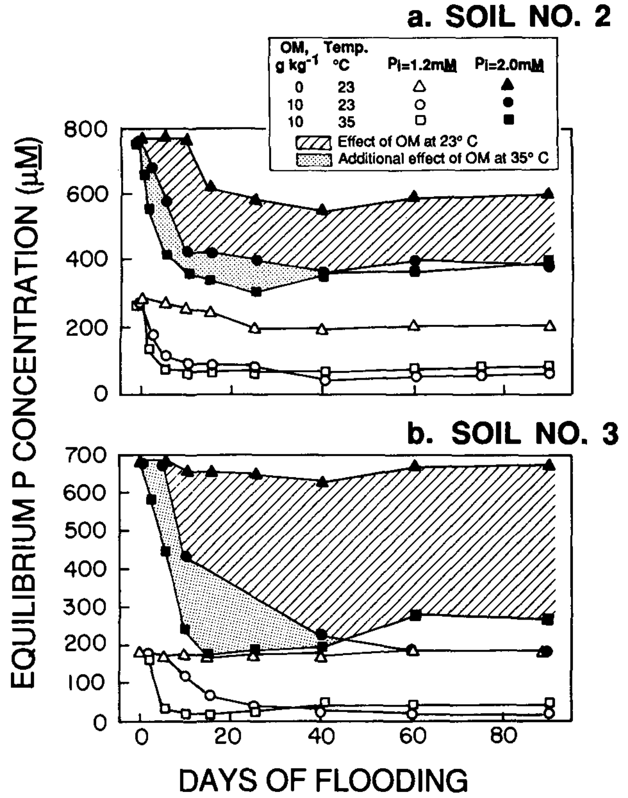

Fig. 1. Effects of flooding period, organic matter (OM), and temperature treatments during flooding on equilibrium (final) P concentrations in flooded-drained Soil 2 and 3 at two P concentrations in sorbing solution ($P_i$).

out of 10 soils (data not shown). These untreated soils contained either low organic C (Soil 3, 5, 9, and 10), low Fe content (Soil 7), or high $CaCO_3$ (Soil 7 and 10) (Table 1). The largest increase in P sorption was noted in Soil 1, followed in decreasing order by Soil 6, 4, 2, and 8 (Table 2). Lack of response to FD conditions in Soil 3 appeared to be due to low OM contents, as it is a noncalcareous soil inherently rich in Fe.

## Effects of Organic Matter and Temperature

### *Effects on Final Phosphorus Concentration*

For Soils 2 and 3, the effects of OM and temperature on $P_f$ were examined at two $P_i$s. When Soil 2 was not treated with OM, FD conditions decreased $P_f$ by up to 31% at $P_i$ = 1.2 m$M$ and up to 22% at $P_i$ = 2.0 m$M$. When Soil 2 was flooded with the OM treatment, the $P_f$ under FD conditions was decreased by 80% and 50% at 23 °C and by 80% and 67% at 35 °C for 1.2 and 2.0 m$M$ $P_i$, respectively (Fig. 1a).

Soil 3 showed no response to FD conditions without the OM treatment (Fig. 1b). We hypothesized that soils with high Fe content, not showing increased P sorption under FD conditions, are possibly deficient in biodecomposable C substrate for anaerobiosis. To test this hypothesis, we included Soil 3 for an oxidation-reduction study. When Soil 3 was flooded without added OM, the redox potential (*Eh*) remained greater than zero even after 40-d FP (Sah et al., 1989). Similarly treated, Soil 1 and 2 showed rapid reduction and attained negative *Eh* values in 5 to 10 d. With added OM (at 23 °C), the *Eh* of Soil 3 decreased rapidly and reached about −200mV in 15 d. At 35 °C, *Eh* decreased still faster. With the OM treatment, the $P_f$ in Soil 3 also decreased rapidly and attained a minimum value in about 60 d at 23 °C, and in only 10 to 15 d at 35 °C. The minimum level of $P_f$ in the OM-treated soil was about 90% lower at $P_i$ = 1.2 and about 75% lower at $P_i$ = 2.0 m$M$, compared with unflooded or OM-treated FD soils, regardless of temperature during FP (Fig. 1b).

When treated with OM at 35 °C, the $P_f$ of both Soil 2 and 3 (Fig. 1a,b) had the tendency to increase with FP after the minimum $P_f$ was attained (sorption peaked). Soil reduction in this treatment was very fast (Sah et al., 1989). The high level of soluble Fe, generated in the reduced zone, diffuses to the surface oxidized zone of a flooded soil, where it is precipitated. Rapid precipitation produces amorphous Fe oxides (Schwertmann et al., 1982). Under similar conditions, the Fe forms in these soils showed good correlation with P sorption. Changes in amorphous FeA (ammonium oxalate at pH 6) correlated best for Soil 3, while that in amorphous FeB (ammonium oxalate at pH 3) gave the best correlation for Soil 2 under each temperature and OM treatment. The free-Fe-oxide fraction showed inconsistent correlation with P sorption under different treatments (Sah et al., 1989). The reorganization of Fe compounds during the later FP, probably reduced the sites or bonding energy for P sorption.

The fact that OM treatment was necessary for Soil 3 to exhibit the response of FD conditions suggests that, in low-OM but Fe-rich soils, OM applied before flooding is necessary to accelerate anaerobiosis during the FP, increasing Fe transformation and resulting in increased P sorption in FD soils.

### *Effects on Phosphorus Sorption*

For both Soil 1 and 6, the OM treatment resulted in a significant increase in EPS under FD conditions without added OM. An increase in the incubation temperature of OM-treated soils to 35 °C increased the EPS to still-higher values only in Soil 6 (Fig. 2 and 3). The effects of OM treatment were similar in both soils; however, the rate and magnitude of the increase in EPS was higher in Soil 6 (Fig. 2 and 3). The higher temperature and added OM significantly decreased the FP required for the maximum EPS for a given $P_f$. For example, for Soil 1 treated with OM, 95% of the maximum EPS was achieved at about 10 d at 35 °C, compared with 19 d at 23 °C and 66 d without added OM. For OM-treated Soil 6, 95% of the maximum EPS was obtained at 65 d at 23 °C, which decreased to about 30 d at 35 °C (Fig. 3).

Organic matter and temperature also resulted in accelerated changes in *Eh* and Fe transformations for Soil 1 and 6. Larger and more-rapid changes in amorphous Fe forms (A and B) and free-Fe-oxide fractions were achieved when the soils were treated with OM and higher temperature (Sah et al., 1989). It appears that OM and temperature treatments affected the redox reactions during the FP, which brought about greater Fe and P transformations and resulted in increased P sorption in FD soils. These treatments re-

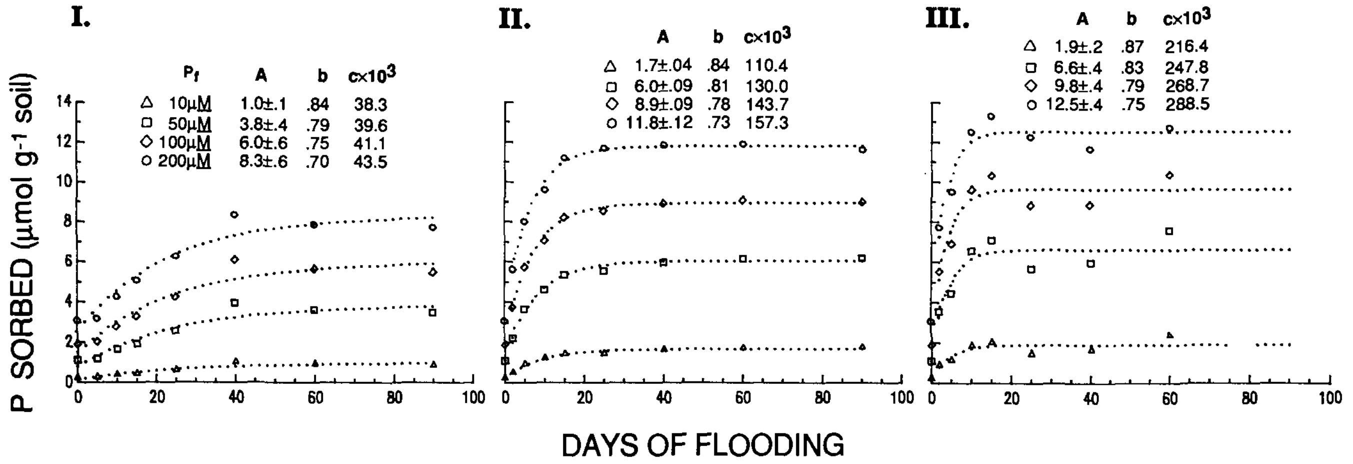

Fig. 2. Effects of flooding period, organic matter (OM), and temperature treatments during flooding on P sorption to maintain an equilibrium (final) P concentration ($P_f$) in flooded-drained soil no. 1. Incubated under flooded condition: I. Without added OM at 23 °C; II. With 10 g OM kg$^{-1}$ soil at 23 °C; III. With 10 g OM kg$^{-1}$ soil at 35 °C. Regression model: $Y = A(1 - b \exp^{-cx})$, where $A$ = maximum expected P sorption, $b$ and $c$ are coefficients, $x$ = days of flooding, and $Y$ = expected P sorption.

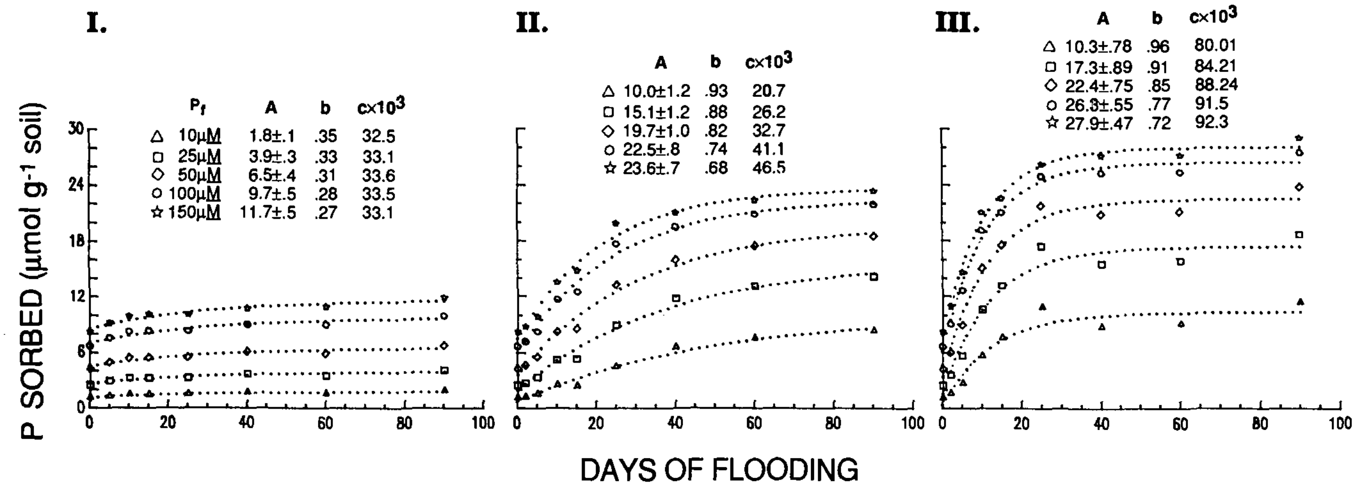

Fig. 3. Effects of flooding period, organic matter (OM), and temperature treatments on P sorption to maintain equilibrium (final) P concentration ($P_f$) in flooded-drained soil no. 6. Incubated under flooded condition: I. Without added OM at 23 °C; II. With 10 g OM kg$^{-1}$ soil at 23 °C; III. With 10 g OM kg$^{-1}$ soil at 35 °C. Regression model: $Y = A(1 - b \exp^{-cx})$, where $Y$ = expected P sorption, $x$ = days of flooding, $A$ = maximum expected P sorption, and $b$ and $c$ are the coefficients.

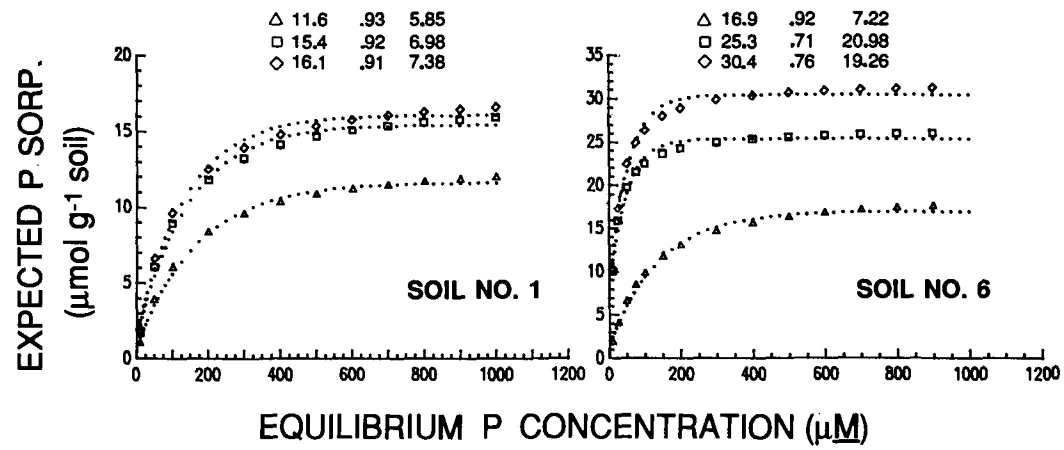

Fig. 4. Effects of organic matter (OM) and temperature on P-sorption isotherms of Soil 1 and 6. The expected P sorption, representing 0.95 of P sorption estimated at the flooding period beyond which P sorption did not increase, is plotted against equilibrium (final) P concentration. Incubation under flooded condition: △ = without added OM at 23 °C; □ = With 10 g OM kg$^{-1}$ soil at 23 °C; ◇ = With 10 g OM kg$^{-1}$ soil at 35 °C. Regression model: $Y = A(1 - b \exp^{-cx})$, where $Y$ = expected P sorption, $x$ = days of flooding, $A$ = maximum expected P sorption, and $b$ and $c$ are coefficients.

sulted in an increase in amorphous FeA and free Fe oxides at the expense of amorphous FeB in Soil 2, whereas, in the remaining three soils, amorphous FeA and B fractions increased at the expense of free Fe oxides (Sah et al., 1989). For Soil 1, OM treatment increased the maximum EPS by 49% at 23 °C and by 64% at 35 °C under FD conditions without OM (Fig. 2). The effects of OM and temperature in Soil 6 were much larger: OM treatment increased the EPS to 231% at 23 °C and to 270% at 35 °C as compared with FD conditions without OM (Fig. 3).

### *Effects on Phosphorus-Sorption Isotherm*

When FD conditions occurred without OM, EPS was maximized (95% of the maximum) at 500 $\mu M$ $P_{\mathrm{f}}$ in Soil 1 and at 400 $\mu M$ $P_{\mathrm{f}}$ in Soil 6 (Fig. 4). As a result of OM treatment, the $P_{\mathrm{f}}$ at which EPS maximized was decreased to 416 $\mu M$ at 23 °C and further to 393 $\mu M$ at 35 °C for Soil 1. For Soil 6, OM treatment decreased the $P_{\mathrm{f}}$ to about 126 $\mu M$, at which EPS was maximized, regardless of temperature. In both soils, OM treatment increased EPS at all $P_{\mathrm{f}}$s and established new P-sorption maxima much higher than those obtained without added OM (Fig. 4).

The FD conditions, particularly with added OM and high temperature during the FP, appears to increase the sites available for P sorption, thereby increasing P-sorption maxima. The maximum EPS values in Soil 1 and 6 increased with OM treatment at 23 °C. However, an increase in temperature to 35 °C produced additional increases only in Soil 6 (Fig. 4). The results of Fe transformation were also similar: elevated temperature (35 °C) produced large additional changes in all three Fe fractions in Soil 6, but these changes in Soil 1 were either small or nonexistent (Sah et al., 1989). These findings suggest that changes in P sorption due to FD conditions are controlled by the changes in Fe fractions.

## CONCLUSIONS

Flooding and draining soils without added OM did not increase P sorption in all soils. Phosphorus sorption in Soil 3, high in reducible Fe, did not increase due to FD conditions without added OM. However, P sorption increased with OM treatment and higher temperature. The soils that had shown variable degrees of increased P sorption without added OM also produced an additional increase with OM and higher temperatures. The OM addition and elevated temperature resulted in a rapid increase in P sorption, causing higher P sorption for a relatively shorter FP.

Flooding for only 2 d was sufficient to increase P sorption in FD soils. However, the FP at which P sorption maximized depended on OM level, temperature, and the nature of the soil. Therefore, these factors must be considered in evaluating the change in P sorption that might occur under FD conditions. Organic-matter treatment and elevated temperatures during soil submergence resulted in higher P-sorption maxima and lowered the FP and $P_{\mathrm{f}}$ at which P sorption was maximized.

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